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Mobile interfaces: Liquids as a perfect structural material for multifunctional, anti-fouling surfaces

Alison Grinthal[1] and Joanna Aizenberg[1,2,3,4]

[1] School of Engineering and Applied Sciences, Harvard University, United States

[2] Wyss Institute for Biologically Inspired Engineering, Harvard University, United States

[3] Department of Chemistry and Chemical Biology, Harvard University, United States

[4] Kavli Institute for Bionano Science and Technology, United States

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Abstract

Life creates some of its most robust, extreme surface materials not from solids but from liquids: a purely liquid interface, stabilized by underlying nanotexture, makes carnivorous plant leaves ultra-slippery, the eye optically perfect and dirt-resistant, our knees lubricated and pressure-tolerant, and insect feet reversibly adhesive and shape-adaptive. Novel liquid surfaces based on this idea have recently been shown to display unprecedented omniphobic, self-healing, anti-ice, antifouling, optical, and adaptive properties. In this Perspective, we present a framework and a path forward for developing and designing such liquid surfaces into sophisticated, versatile multifunctional materials. Drawing on concepts from solid materials design and fluid dynamics, we outline how the continuous dynamics, responsiveness, and multiscale patternability of a liquid surface layer can be harnessed to create a wide range of unique, active interfacial functions - able to operate in dynamic, extreme environments - not achievable with static solids. We discuss how, in partnership with the underlying substrate, the liquid surface can be programmed to adaptively and reversibly reconfigure from a defect-free, molecularly smooth, transparent interface through an infinite range of finely tuned liquid topographies in response to environmental stimuli. With nearly unlimited design possibilities and unmatched interfacial properties, liquid materials - as long-term stable interfaces yet in their fully liquid state - are likely to transform surface design everywhere from medicine to architecture to energy infrastructure.

1. Introduction

A living organism can pack, orient, weave, and sculpt some of the most intricately structured optical, mechanical, and multifunctional solid materials known. But sometimes nature takes a break and appears to forget about solids altogether. Instead, it meets some of life's toughest challenges with surface materials made entirely of liquids tumbling and sliding over the surface, constantly moving, bouncing randomly between the bulk and the surface, with no fixed molecular positions at all (Figure 1). A purely liquid layer creates the ultra-slippery slide into carnivorous plants' stomachs, remaining sturdy as a parade of insects, even lizards, land and skid down[1]. The liquid film on our eyes provides a perfectly smooth refractive surface, is continuously adjustable just by squinting, and at the same time keeps away dirt and bacteria[2]. Tear films work equally well for fish swimming through salty, sandy oceans with no eyelids[3], a single design handling rapid pressure changes as they poke their heads above the surface or scan for predators with eyes half in, half out[4]. A thin liquid film on pounding knees is all it takes to keep our bones gliding smoothly past each other[5], while insects can grip and run along any terrain thanks to the infinitely adaptable shape of a liquid film on the soles of their feet[6]. A similar liquid film on tree frogs' toes simultaneously adjusts to changing surfaces and hopping impacts and even makes it possible to climb over dripping leaves and flooded rocks[7].

But just microns or less from the pounding, shearing, and other forces outside, the liquid's other side is attuned to a completely different set of forces. Integrated into an

intricate underworld of micro- and nanoscale labyrinths, networks, and pores, sculpted into tiny liquid architectures, its inner surface is acutely sensitive to capillary, electrostatic, van der Waals, and osmotic forces arising from its contacts with the underlying solid (Figure 1, insets). An optically perfect tear film belies a cornea packed with folds, ridges, and projections patterned by habitat: dense, interconnected labyrinths and whorls stabilize fish films against aquatic pressures[3], with especially dense structuring for species that go in and out[4]. Even as cells die, forests of microvilli on the mammalian cornea orchestrate the disturbance into localized pattern, density, and chemical changes[8], enabling the liquid to handle the rest by flowing into the gaps to maintain an intact outer surface. Joint fluid subjected to bone on one side is infused in an elastic cartilage network on the other – under pressure, the film deforms the cartilage, deformation changes the microscale roughness, and the fluid flows over, in, and out of the network, the cooperative endeavor coordinating the outer surface's response[5]. An insect's foot film balances capillary forces from the outer terrain with those inside an underlying elastic cuticle network, precisely regulating the film's outer topography and minimizing liquid lost as footprints[6]. But always, through everything, the liquid's molecules are continuously tumbling, shuttling between the underlying network, the film's interior, and the outer surface, uniting them through constant motion.

Clearly liquid surfaces play an indispensable role in living systems, and produce a wide spectrum of multifunctional, dynamic properties that have eluded synthetic technologies, even "fluid-like" molecular and nanofibrous coatings[9-14]. We use liquid layers all the time for lithographic printing, coating, device fabrication, heat transfer, and lubrication, but these ultimately dry, cure, evaporate, or remain enclosed; when it comes

to structural and long-term surface components, we prefer materials that are solid, static, and therefore highly predictable and manufacturable. The problem long keeping liquids as *structural* materials off our materials radar screen, of course, is that their dynamics are extremely complex and sensitive to environmental conditions. However, it's not obvious that life handles liquids fundamentally differently from any of its other materials. Molecules turning over on various time scales are the norm in living systems: at surfaces and everywhere else, "materials" consist of proteins continuously associating and dissociating, DNA winding and unwinding, membranes pinching and fusing, cell structures collapsing and reforming, even bone matrix forming and dissolving, with liquids and solids structured together and moving in tune with each other. Indeed, many of our bioinspired strategies for designing solid materials already demonstrate fine control over liquids, since liquids are almost invariably present in these systems and the process often turns out to be an exercise in controlling their flow, capillary forces, surface tension, and structuring[15-19]. While microfluidics, nanofluidics, and thin film dynamics aren't geared toward developing liquids as long-term surface materials, these burgeoning fields are also providing theoretical and experimental insights into how a rich range of controlled liquid behaviors can be generated in the context of structurally and chemically tailored solid substrates[20-22].

With these ideas, tools, and needs converging from all directions, the time is ripe for liquids to enter the scene as full-fledged dynamic surface materials. Indeed, several very recent studies of omniphobic, self-healing, anti-ice, antifouling, optical, and adaptive liquid surfaces have already begun to transform materials fields across the board[23-31]. In this Perspective, building on the insights and intriguing questions arising

from this work as well as concepts from solid self-assembly, tribology, and fluid mechanics, we outline a framework and a path forward for developing, designing, and, not least, even thinking about liquids as complex functional materials. To start, we present an operating definition of bottom-up design, a strategy that as commonly understood makes no sense for liquids but which is crucial for conceiving and realizing their full functional potential. We then discuss liquids as dynamic, active surface materials, and identify the fundamental tasks design must address to develop this core property into increasingly sophisticated functions operating in changing, often harsh environments. At the heart of design, we discuss how structural and chemical features of a solid substrate can be tailored to "template" or shape the liquid's multiscale dynamics and responsiveness, and how making the template itself dynamic expands the possibilities for adaptive, responsive behaviors even further. The concepts developed in turning liquids into versatile surface materials expand our thinking about solid materials design as well, deepening our vision for integrated dynamic, multifunctional materials built from solids and liquids working together.

2. Defining "bottom-up" for a liquid

Taking a "bottom-up" approach to materials design – building on and taking advantage of the starting components' most basic properties – has proven transformative across many fields as a way to engineer diverse and previously unimaginable materials properties from first principles. This concept is essential to thinking about any new material – it allows us to see as far and wide as possible the potential for what the

material can be and how to go about designing and constructing it to make the most of its unique possibilities. But in practice, it also immediately lands us in a quandary if our material is a liquid. Building from the bottom up has almost invariably come to mean progressing from small to large and dynamic to static: starting from molecular or nanoparticle components and ordering and assembling them in different ways to create different fixed, final products[32]. But this approach would obviously defeat the purpose of using a liquid – if we were to progressively order, assemble, and immobilize its molecular components, we would lose, not build on, the intrinsic, ongoing dynamics that inspired us to develop it as a material in the first place.

Certainly we can make some headway toward designing a liquid surface's properties by specifying its molecular composition, but this alone won't get us very far toward developing it as a viable or interesting material. To consider what it might look like to design, tailor, and optimize a full splendor of liquid surface material properties, we therefore take a deeper look at what bottom-up design consists of. As mentioned, "bottom" traditionally refers to the shape and other properties of the system's components. But more fundamentally, what these properties actually do is collectively determine how the system takes various driving forces and translates them into a response. This can be the association and ordering of the components, but from a system perspective it could be any change in shape or motion, within the internal fine structure, as a whole, or both. This broader operating definition of bottom can cover not only liquids but also the design of dynamic solids – and may also relate to how life handles its gamut of dynamic liquid and solid materials. Here, we define the bottom for a liquid not as any particular shape or form but as its continuous thermal responsiveness and mobility.

This is the basic starting point we build on, and is the property that gives liquid materials their unique behaviors and ultimately makes them more, not less, designable.

Following this framework, we define "up" as evolving not toward a particular final structure but toward more sophisticated responsiveness to various forces. This can mean, for example, responding to pressure or temperature gradients or dragging feet with specific types of small-scale flows. But just as importantly, it can also mean designing the system not to respond to certain forces, such as gravity or shear. In general, then, design focuses on organizing how the liquid moves and doesn't move on different scales in the context of the many forces it encounters – hence tailoring it for a variety of functions that make full use of its dynamic capacities yet simultaneously making it robust enough to act as a strong, stable material. In practice, this version of bottom-up design is facilitated by a solid substrate similar to the architectures that underlie the liquid surfaces in the living systems. As we discuss in Section 4, the substrate works somewhat analogously to the template in other self-organizing systems, but the liquid material can be redesigned at any time, for example if the substrate itself changes.

3. Cultivating perfection

3.1 From the bottom: dynamic perfection

Right from the start, a liquid's "bottom" state brings an intrinsic property almost no other material can achieve: defect-free perfection. With continuous molecular mobility, a liquid on a solid substrate – with the exception of highly viscous or semi-

crystalline fluids - is free to organize its surface into a molecularly smooth, homogeneous, energy-minimized state, avoiding the kinetic traps that almost inevitably produce defects in solid materials. As on the eye, a liquid surface can be smooth down past the smallest wavelengths of light: with no defects to scatter light at the interface, a liquid film on an index-matched substrate is perfectly transparent to all visible (Figure 2A) as well as IR wavelengths[24,29,33]. Moreover, robust self-healing is built into the definition of this dynamic form of perfection. Since perfection is an active process – with the surface continuously forming and regenerating – it naturally restores itself through molecular turnover and local flow. Following even macroscale damage to the interface or the underlying substrate, a liquid surface instantly self-heals, erasing any sign of the disturbance within milliseconds[24] (Figure 2B).

Surface perfection, not to mention self-healing, is of course highly coveted in nearly every field: even tiny chemical and topographic defects can have a major impact on liquid pinning and drag[10,34,35], ice adhesion[36], bacterial colonization[37,38], dirt buildup, and just about any other dynamic process taking place at the interface. But as soon as we start interfacing such processes with the liquid surface, its ability to act as a defect-free interface in practice potentially becomes more complicated. The surface now has to act perfect in the face of things exerting nontrivial forces – sliding, dragging, poking, and stepping on it. Certainly the liquid surface's ability to actively and continuously restore itself should serve it well in this context, but it's no longer necessarily enough for it to regain its function even milliseconds after any of these assaults.

And yet it does act defect-free (Figure 2C). On recently reported liquid interfaces, droplets of all different sizes, surface tensions, compositions, and interfacial tensions

slide freely, with tilt angles of just a few degrees, minimal contact angle hysteresis, and none of the pinning or stick-slip behavior seen with even molecular scale defects[23,24,39]. Complex substances such as ketchup and blood – each a distinct mix of fluids, polymers, and particles – similarly slide unimpeded[24], despite the complicated slew of multiscale forces and interactions all acting on the surface at once. Likewise chunks of solid ice can easily slide or be dragged along the interface[24,27] – if the raindrops and condensation have time to freeze at all before escaping. Even bacteria[26] and insects[24], notorious for their exceptional ability to colonize and attach to any surface, find no way to adhere, as they poke, prod, and attempt to grasp the liquid interface using various appendages and molecular attachment mechanisms. Furthermore, the surface can manage all of this against a backdrop of shear flow, changing temperatures, high atmospheric or submerged pressures, or other forces from the environment. These displays of robustness and negligible resistance are rarely seen in traditional synthetic or even natural materials, individually let alone all at once.

3.2 The task for design: perfection as responsiveness

Herein begins the task for design. To make use of a liquid's inherent perfection in the context of so many dynamic functions, we can't take it for granted – the system must be designed to actively cultivate it and adapt to the changing environment. As we discussed in Section 2, this is where the solid substrate comes into play. In practice, even the basic smooth surface and its robust self-healing depend on the liquid's ability to wet and spread on the solid. But, as we might expect, it turns out that a flat chemically

tailored substrate isn't sufficient in the more complex situations described above: for the liquid interface to act perfect toward dynamic droplets, bugs, and substances, we need to give the underlying substrate an appropriate 3D nano/microstructure as well[23,24,26-28,33,40]. As in the living systems, the material's function relies on balancing forces at its outer interface with forces from its inner surface contacts.

Moreover, several lines of evidence suggest that, far from being just a prerequisite for maintaining topographic and chemical homogeneity under duress, the responsive dance between the surface and everything on it may be the heart of how perfection works. Ants can adhere to a highly smooth surface with forces one hundred times their body weight[41] but can't stand still on the liquid film; bacteria rapidly overgrow virtually every solid surface[42], with the static state nearly the only criterion, but show practically zero growth or even attachment here; a sliding droplet's contact line is thought to be actively moved along by the dynamic functional groups on fluid-like monolayers[43]. Thus liquid surfaces may achieve functional perfection by an inherently dynamic, responsive mechanism that requires us to reconsider what it means to be a perfect surface. An essential component of design, then, may be to begin to understand what kinds of motions matter – for example, how far the liquid is carried along, and how this is balanced with stabilizing the surface against loss. Understanding such features of material function may in turn provide even greater opportunities to design not only "perfect" but directed, selective functions as well.

4. Templating a material in perpetual motion

For perspective on how to design liquid materials, we go back for a moment to consider how living and bioinspired systems achieve precise, detailed control over the assembly of solid materials. In many cases a structured template – similar to the microarchitectures underlying biological liquid surfaces – has been shown to play a crucial role in shaping these systems' dynamics[44-49]. Although not a direct blueprint – the components' own attractions and bulk mechanics do most of the work – the template participates in shaping the flows, gradients, and motions of chemical species and particles by modifying the forces they feel. It does this by several means. First, it presents specific, often spatially patterned, surface chemistries. Strictly speaking, these functional groups only contact a tiny fraction of the components at the interface, but they can profoundly influence intramolecular dynamics and mobility throughout the rest of the system, as well as impose constraints on the mechanical behavior. Controlling the surface-to-volume ratio via micro/nanostructuring can further amplify the influence of the direct template interactions relative to the system's internal and outside forces. In particular, structured micro/nanoenvironments – with geometry, size, and spacing that complement the system's intramolecular effects and bulk mechanics – can produce a phenomenal range of specific, complex dynamics, with local control and multiscale patterning. As we will see, these principles can be carried over almost directly to the design of robust yet continuously mobile liquid materials.

4.1 Thin film dynamics, manipulation, and dilemmas

On a flat substrate, liquids already display a fascinating repertoire of dynamic behaviors as thin films. At only microns or nanometers thick, thin films have been shown to display exquisite sensitivity to a variety of forces, responding with intricately patterned multiscale motions and flows (Figure 3). Gravity, thermocapillary forces, elasticity, chemical interactions with the substrate, or substances moving on the surface produce unique forms of instabilities that can propagate in two or even three dimensions – transiently creating, for example, local regions of patterned surface contour or focused thinning[21,50-54]. Extensive study and modeling of these phenomena, fundamentally and in the context of printing, coating, and other applications, has produced a diversity of approaches to manipulating these dynamics down to the nanoscale. Chemically patterned substrates have been used to create a wide range of thin film behaviors by imposing complex wettability gradients[55-57], while combining surface patterning with thermally imposed shear stresses at the liquid-air interface has been shown to generate controlled flow and wetting behaviors[54,58,59]. These approaches have been complemented by the manipulation of film energetics and morphology by electric fields[60,61]. Complex molecular interactions of polymer films at the liquid-substrate interface, as well as evaporative convection patterns of multicomponent liquids, are yet another source of diverse behaviors[62,63]. The short distance between the film's two interfaces – substrate and outer – combined with its own minimal thickness leads to an especially sensitive dynamic coupling between bulk, substrate, and surface forces[21]. For example, a fluid flowing over the outer surface induces coupled motion of the film surface, leading to local thinning and enhancing sensitivity to substrate interactions, which modifies the film's local mobility and in turn modifies the motion of the flowing fluid.

These responsive dynamics coupled to the properties of an underlying substrate suggest abundant possibilities for design, but a flat "template" nevertheless has substantial limits. With two-dimensional surface chemistry as the only means of built-in control, the system is stymied by several dilemmas. First, dynamics and stability are directly opposed to each other: stabilizing the film against gravity and other body and surface forces, as by making it thinner, comes at the cost of increasingly solid-like behavior[64]. In addition, although a thinner film is more stable against gravity, its increasing sensitivity to molecular interactions with the substrate can simultaneously make it more vulnerable to dewetting or rupture if its chemical wettability is any less than perfect[51]. The two-dimensional system also puts conflicting demands on the liquid's surface tension: the surface tension must be low to keep the film flat rather than beaded, but at the same time it should be high to resist the deformations associated with gravity or shear-induced flow. Since all of these dilemmas place strong restrictions on the choice of liquid chemistry, they also restrict the capacity to specify how the liquid interacts with the many different substances that contact its surface in an open environment.

4.2 Resolving in 3D

Micro/nanostructuring the liquid's substrate interface in 3D makes it possible to resolve these dilemmas by introducing complexity, compartmentalization, and micro/nanoscale effects while maintaining a continuous film on the outside[22,39,65,66]. A structured substrate provides a common mechanism to enhance both stability and dynamics at once: infusion into underlying pores allows greater bulk dynamics by locally

increasing the thickness, but also stabilizes the film through capillary effects[67]. Roughness can also simultaneously decrease susceptibility to both gravity and dewetting, since the apparent contact angle of an infused liquid approaches zero even if chemically the liquid is only partially wetting, introducing a so-called superlyophilic state. Structuring also effectively buffers the delicate balancing act for surface tension, by not relying on chemistry to do all the work in keeping the outer surface shape stably molecularly smooth and defect-free. Micro/nanostructuring the film's underside, then, frees us to think much more broadly about specifying the liquid's interactions with substances on the surface. Like the 2D wettability gradients introduced by chemical patterning, 3D topographic parameters have been modeled and used to manipulate thin film flow and morphology[68], with additional complexity introduced by thermally induced surface forces[69], greatly enhancing the possibilities for precise control and design.

Structuring also directly unites liquid materials design with the vast array of strategies for designing solid micro- and nanoarchitectures – many of them intricately patterned and controlled by bioinspired systems themselves (Figure 4). Random fibrous networks as common as Teflon, or even polymer gels, can, if chemically functionalized, provide the porous texture to hold an infused liquid[24,70]. Uniformly nanoscale texture can be created directly on a wide range of surfaces by a simple reaction that produces nanocrystalline metal oxides, such as aluminum oxy hydroxide, boehmite (AlO(OH))[28,71], with many options for varying the crystalline properties and photo-patterning the surface[28]. But we can also introduce precise, highly ordered, yet practically unlimited geometries with controlled shape, periodicity, anisotropy, defects, and hierarchy by methods built on high-aspect-ratio anchored fiber arrays or colloidal crystal synthesis.

Fiber arrays can be created and replicated in materials from ceramics to soft polymers, even further sculpted into arbitrary shapes and surface-wide gradients via polymer electrodeposition, and/or self-assembled – through dynamic interplay with liquids – into chiral, hierarchical structures[72,73]. Highly ordered inverse colloidal monolayers provide closed-cell geometries and uniform pore sizes, with options for introducing controlled defects and patterning through topographic templating and for spatially patterning the surface chemistry[33]. Once functionalized with liquid-specific surface chemistries, any of these substrates can form a basic template to hold a liquid layer – providing a library of possibilities to systematically study and optimize how different features translate into liquid dynamics, responses to different forces, and functions of the outer interface.

4.3 Micro/nanostructuring liquid functional behavior

These architectural strategies, combined with the wealth of insights into liquid behavior coming from the fields of fluid mechanics, microfluidics, and tribology, provide an extremely rich source of tools and concepts, which potentially enable us to intricately shape how the infused liquid confined in the underlying solid will function and respond when continuously subjected to diverse environments and substances. The possibilities have only begun to be tapped, but the early work demonstrates that the robust behavior as a stable surface material can be achieved by incorporating the full diversity of ideas into materials design.

For example, the substrate's geometry, dimensions, defects, and multiscale organization can, together with chemistry, radically alter the specific deformations a response to specific shear forces will entail. On a flat substrate, gravity or shear forces

generally drive flow by inducing large-scale curvature of the liquid surface. But if the liquid is infused in a uniformly nanostructured substrate, the curvature changes must now be negotiated locally within each nanocompartment, with nanoscale menisci that can substantially raise the energy cost of flow. Due to the strong capillarity, a liquid film entrapped in such substrates resists flow and remains stable under extremely high shear forces[28,33] (Figure 5A, top), enabling it to remain fully omniphobic even after such exposures. The spacing is critical to setting the response threshold. On a hierarchically structured substrate, the liquid does flow between microstructures at intermediate forces but remains stable within the nanostructures overlying them, carving out an undulating but continuous liquid surface[28] (Figure 5A, center). The differential sensitivity threshold for the two feature sizes is consistent with the liquid's effective capillary length, a force-dependent measure of the length scale at which body forces can overcome surface tension, and can be tailored to evoke force-specific effects on the surface's repellent behavior[28].

By introducing defects into the nanostructured surface, we can change not only the sensitivity but also the type of response to shear. A microscale defect within a field of uniform nanostructures effectively creates a low-aspect-ratio pore where the film is microns wide and nanometers thick. As discussed in Section 4.1, such a thin film, without interspersed nanostructures, is especially sensitive to molecular interactions with the substrate. As a result, the liquid can respond to intermediate forces by highly localized dewetting within the defect. The intrinsic contact angle now plays a crucial role. As mentioned in Section 4.2, the effective contact angle on top of the surrounding nanotextured region is zero, but as the overlying film thins, this collective effect will no

longer apply within the comparatively wide defect. Around the edges, then, the liquid can begin to take the shape favored by its intrinsic contact angle – effectively migrating away from the center as the force increases[33] (Figure 5A, bottom). The sensitivity of this response – and how it balances with other response modes such as those described above – can be set by the combination of the intrinsic contact angle and the relative dimensions and pattern of the intact and defect geometries. Modeling this process has allowed us to precisely correlate defect spacing, film dynamics, and omniphobic performance under a variety of shear conditions.

Combining spatially patterned chemistry with patterned topography provides a highly precise way to orchestrate how and where the liquid film can be pushed by – and can push – a second liquid on top of it, even for low-surface-tension liquids that are not well-controlled by chemical patterning alone. On a uniform nanotexture, for example, a defined region can be functionalized with a surface chemistry that the liquid film wets only moderately, with strongly wetting chemistry everywhere else. Alone, the liquid film will still wet the entire substrate, since the roughness itself enhances the wettability. But if another fluid with better wettability in that region – a simple polar or apolar liquid, or a complex substance like blood or crude oil – flows over the film, the original film now becomes only metastable in the patterned area. Over time, the film will be displaced by the second fluid and redistribute to the surrounding region. But the pushing stops there – outside the patterned region, the film is thermodynamically stable: surface chemistry and capillarity resist further movement, and the film pushes back on the second fluid to keep it confined[33] (Figure 5B, top). This not only creates a time-dependent way to pattern the behavior of the second substance, but the same principle can also work in reverse. If the

film is forced out of a region that it does wet preferentially, it will push the second substance out and flow back to form a continuous film again (Figure 5B, bottom).

4.4 Integrating local and global

Yet the possibilities for shaping the film's functional behavior are even richer than the sum of all these local negotiations. Since the liquid film is continuous over the whole surface, everything discussed so far is integrated by how it can move and communicate among the compartments, both within and on top of the texture. The film's response to gravity, for instance, depends not only on how the liquid can deform locally but also on how freely it can snake among the roots of the nanoforest (Figure 5C, left). This underlying flow entrains the film's dynamics at the surface, substantially altering the kinetics of its response[74]. The structures' height and spacing once again play a critical role: setting these parameters tunes the liquid's effective viscosity within the texture, providing a way to specify large-scale liquid kinetics through substrate architecture. A complementary way to tune the kinetics, with fewer restrictions on the spacing per se, is to use closed-cell architectures. Porous substrates, with arrays of individual holes patterned by colloidal spheres (Figure 4, right), allow little or no flow within the plane of the texture (Figure 5C, center). Liquids infused in such structures are extremely resistant to gravity even with microscale pore diameters, showing no perceptible signs of flow after months under continuous gravitational force[33].

Even if the liquid is trapped within disconnected compartments, however, the underlying architecture can still shape collective multiscale dynamics in ways that differ

substantially from purely additive effects. Since the film is necessarily thicker within wells than on top of the walls between them, a bird's eye view of the surface can show distinct dynamics directly on top of, compared to between, compartments. Yet even if the film over the walls becomes too thin to sustain intrinsic dynamics by itself, the length scale of the overall surface dynamics has been found to be several times larger than the diameter of the wells[75]. This implies that the dynamics arising from within the wells can propagate across even supposedly impassable barriers (Figure 5C, right). The periodic geometry still plays a central role in defining this length scale, but the collective behavior can undoubtedly be tuned by other structural parameters as well, such as pore depth, wall dimensions, and surface chemistry. The mechanism is still under investigation, but this unexpected form of connectivity gives an even broader taste of the potential complexity and specificity that can be designed into liquid-bearing materials.

5. Adaptive liquid surfaces: dynamic dynamics

5.1 Template takes an active role

With increasing sophistication, then, the liquid material adapts and responds to stimuli all the time as part of its ongoing function and self-maintenance. But as we mentioned in Section 2, the liquid's continuous dynamics make the system inherently meta-responsive as well: its responsiveness profile itself can be redesigned any time in response to specific stimuli and changing conditions. To build this capacity into adaptive materials, we look again to the template design. Elastic substrates have been shown to

introduce complex liquid film dynamics[76,77], with elastic topography[78,79] and porosity[80] introducing further multiscale responses. In addition, recent interest in stimulus-responsive materials has produced an ever-growing assortment of dynamic, elastic solids that reversibly change size, shape, or even surface chemistry in response to mechanical, chemical, temperature, magnetic, electric, light and many more types of stimuli[81-85]. With these, we can design the substrate architecture itself to come alive in response to stimuli and translate all kinds of signals from the environment into its multiscale language of capillary, electrostatic, and other forces. For example, mechanically stretching, bending, or poking an elastic substrate creates unique surface-wide stress fields that, in a porous architecture, translate into sensitive, specific changes in pore size, shape, spacing, and potentially connectivity. These in turn create stimulus-specific pore pressure profiles (Figure 6A) that are felt by the infused liquid[29].

The liquid, for its part, responds by doing what it does best – it flows, redistributes, and reconfigures locally within each pore and over the continuous film in predictable, detailed, sensitive ways to find its new thermodynamically stable shape. As we model for a prototype array of nanopores (Figure 6B), this reshaping follows a progressive path as the stress is increased[29]. Initially, the film simply becomes thinner, maintaining a smooth outer surface by redistributing above the pores just as it self-heals in other cases. But as its outer surface approaches the level of the structures, it begins to curve inward over each pore as the inward pressure from the widening pores starts to overcome the surface tension. These deformations produce a gently roughening liquid surface. At higher stresses – with more stretching, wider pores, and more inward pressure – the inward curvature and thinning continue, as the liquid's outer surface increasingly

takes the shape of the substrate. The combined dynamic responses of the template and liquid thus reconfigure both the inner and outer liquid interfaces, as well as the film's overall depth profile – creating a whole range of new liquid architectures with corresponding new dynamics.

5.2 Tuning the motion of droplets and light

To a foreign droplet traveling over the liquid interface, these increasingly rough topographies no longer look or act perfect, and the droplet accordingly stops in its tracks as the material is stretched[29] (Figure 7A, left). But as soon as the stress is released and the pores regain their original dimensions, the liquid film immediately returns to its original defect-free perfection, and the droplet continues on its way. In fact, this entire reversible "pinning" process – not just the film's behavior in the smooth slippery state – turns out to be yet another twist on the film's ability to act perfect toward things moving on it. In almost all other cases where pinning is induced by a switch in surface properties, the droplet irreversibly transitions from a metastable state – such as balanced on an air/solid interface – to a stable wetting state[86-90]. Even if the surface properties can easily be returned to their original configuration, the droplet can't: it remains trapped in place. On the liquid interface, no such transitions are involved. The film's surface and the droplet's underside progressively develop curvature together and conformally follow the underlying topography as a continuous liquid-liquid interface – and just as smoothly return to the flat state together. The situation is no different for a second droplet placed on the surface once it's already stretched. Together the droplet and film reach the same

mutually stable curvature, and both droplets begin sliding at precisely the same moment as the interface returns to its original flat state (Figure 7A, left, bottom row).

This smooth transition, with thermodynamic stability all along the way, can also be stopped at any point – allowing a precise, graded response to stress[29] (Figure 7A, right). The surface can be adjusted to anything from perfectly slippery, through a continuous range of intermediate slipperiness – as measured by the amount of tilting required for droplets to slide – to complete pinning and back, by subtly varying the degree of stretch. The fine resolution between degrees of slipperiness also underscores that each of the topographies is still perfect, defined by smooth, albeit curved, liquid precision. In addition, the fine tunability of the "responsive responsive" surface makes it possible to resolve subtle differences between different types of droplets. In the flat, relaxed state, the surface acts perfect toward droplets of all surface tensions, letting them all move freely. But since the exact topography under a given amount of stress depends on the balance between pore changes and surface tension, droplets with different interfacial tensions will each see a slightly different degree of curvature. These differences give each droplet type a characteristic sensitivity threshold and response profile[29] (Figure 7A, right), determined by the combination of pore features, stimulus strength, and interfacial tension.

The fine resolution and liquid precision of these inducible topographies simultaneously allows the precise manipulation of light[29]. Not only different degrees but also different patterns of mechanical stress induce characteristic transitions from transparent to opaque, and back. These transitions can be highly localized: bending or poking the transparent flat surface creates an opaque region along the crease or poked

spot, with boundaries and spatial gradations that correlate with the predicted pore pressure profiles (Figure 7B, left). The extent and sharpness of these spatial gradations will be determined not only by the nature of the stimulus but also by the connectivity and length scale of liquid mobility. Just as for slipperiness, graded degrees of planar stretching create graded, finely tuned degrees of optical transmission, with graded reversibility as the surface is relaxed (Figure 7B, right) – in direct parallel with the transition between smooth and rough topography (Figure 7B, right, insets). Combined with the order, patterning, and nanoscale control offered by inverse colloidal architectures in particular[47,91], these responsive liquid behaviors can potentially be designed to sculpt air-liquid interfaces that create a wide range of color, pattern, and other optical responses.

5.3 Stimulus-responsive liquids

The liquid properties, too, can be made directly tunable by a variety of electric, chemical, temperature, magnetic, and other stimuli. Depending on the specific composition of the liquid, an electric field can potentially alter its intermolecular interactions, both within the liquid and at its two interfaces – altering its wetting strength and its overall dynamic interplay between body, substrate, and surface forces[92]. The same can be said for a wide range of chemical signals, from pH to salts, alcohols, or specific biomolecules. While liquids can specifically be chosen not to respond to cold or heat, others can be designed to respond to temperature changes within a particular range with sensitive variations in viscosity or surface tension. Temperature stimuli can, for example,

lead to adjustments in the velocity of droplets moving over the surface[30]. Ferrofluids – liquid suspensions of magnetic particles – introduce a particularly interesting set of magneto-responsive behaviors: a magnetic field can overcome surface tension and other forces to dramatically reshape the liquid surface[93]. The molecular groups and particles underlying these stimulus sensitivities need not even be that different from those of the responsive solids – but together, responsive liquids and solids provide vastly different and complementary routes for translating diverse stimuli into adaptive changes in the liquid material's properties.

6. Outlook

The primary purpose of this Perspective Article is to provide direction for a new materials approach that uses liquids as a structural material for the design of robust, multifunctional interfaces. The liquid surfaces we discuss derive a very wide range of omniphobic, antifouling, optical, healing, and adaptive functions specifically from remaining in the fully liquid state, yet act as long-term, stable surface materials exposed to changing, unpredictable, or extreme environments – and therefore may require quite a different set of design concepts than traditionally studied liquid films that harden, evaporate, or are sandwiched between highly controlled solids. With the surge of interest in developing this strategy for practical use across many fields, we believe it is critical at this early stage to frame liquid surface materials in terms that emphasize common ground and potentially stimulate cross-pollination across many areas of materials design,

including thin films, tribology, fluid mechanics, microfluidics, and self-assembly, and to emphasize the role of materials chemistry in all these approaches.

By placing never-ending motion at the root of design, liquids take us into a completely new realm for creating and understanding interfacial materials. A liquid surface not only intrinsically builds in a wide range of dynamic functions – self-healing, self-organizing, self-cleaning, self-shaping, self-adapting – but fundamentally unites all of them down to the molecular level. It's no coincidence that many of them can be defined as "self": with the liquid's molecules in continuous thermal motion, a tremendous variety of surface functions that generally require energy input can be powered by ambient thermal energy alone. Based on the design principles outlined here, these unique capacities – common to all liquids – make it possible to create multifunctional, responsive, autonomous surface behaviors from the bottom up. But even more crucially, they also challenge us to think about such behaviors in ways we hadn't imagined. All kinds of dynamic interfacial phenomena – from substances sliding, to cells growing, to crystals and particles assembling – can and must be conceived not only in terms of fixed surface properties but also as active, multiscale interplays with a dynamic, defect-free, molecularly smooth surface. Incorporating this active dimension into surface design will likely be inseparable from developing new understandings of the phenomena themselves.

On the liquid's underside as well, designing the liquid-substrate interface as an active, mutual interplay between liquid and solid can open even wider frontiers in creating complex liquid material functions. Several recent systems are already beginning to show how this can work at the nanoscale, with functionalized particles[84] and fiber arrays[72] dynamically assembling, disassembling, and reorganizing as conditions change.

Indeed, these as well as many other assembling systems are all the same story of a two-way interplay between solids and liquids: liquids order solids and enable them to move, and solids shape the topography and flow of liquids[19,76-79] – even breaking down the distinction between template and templated in favor of mutual coassembly[17]. Incorporating this dynamic interplay into the liquid material would not only create more complex, responsive behavior at the liquid's outer interface – as in several of the living systems – but would provide opportunities to integrate the substrate's and the liquid's complementary responses to stimuli.

With these nearly unlimited design possibilities, and the diversity of unmatched properties that have already been demonstrated, liquid materials can fundamentally transform how we design surfaces everywhere, from medicine to airplanes to buildings. Fluid transport systems – from fuel to heating pipes to drinking water to dialysis tubing – can be designed to minimize drag, fouling, and corrosion, to withstand strong shear, high pressure, and high temperature, and even to self-regulate flow based on stimuli from the environment or the transported fluid. Planes, wind turbines, and refrigerators can be designed to simultaneously shed condensation, minimize ice nucleation, and prevent ice adhesion, with shear and gravity acting as an aid to self-cleaning rather than a threat to surface integrity. Optical devices and windows can self-adjust light transmission as well as self-clean, while multifunctional tent fabrics can be envisioned that adapt both transparency and water shedding for dry and sunny or dark and rainy weather. With infinitely reconfigurable liquid topographies, dynamic, defect-free liquid interfaces can themselves serve as novel templates for a wide range of microfluidic, lab-on-chip, and materials synthesis systems. By combining continuous flow and turnover with multiscale

precision and control, liquid materials – never drying, never hardening, and fully exposed to the changing and extreme conditions of diverse environments – may offer radically new opportunities for creating dynamic, responsive, energy-efficient materials needed to meet our most pressing materials challenges.

Acknowledements

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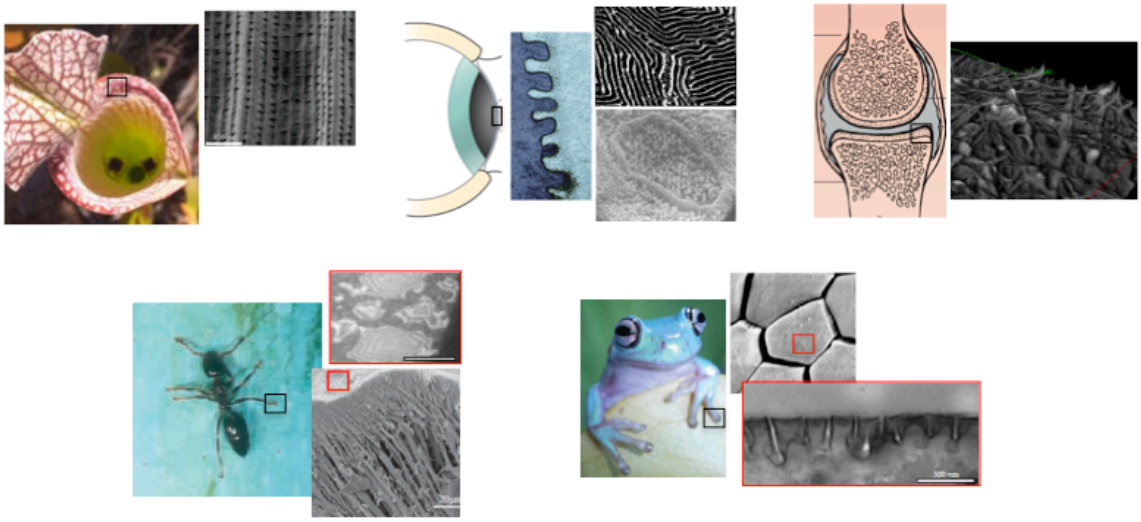


Figure 1. Liquid surfaces rooted in porous architectures. A purely liquid interface creates (top) the ultra-slippery surface of the carnivorous pitcher plant leaf; the optically perfect, antifouling, pressure-resistant surface of the eye (Adapted from ref.[2]); the lubricating surface between bones (Adapted from ref.[5]); (bottom) the shape-adapting soles of insect feet (Adapted from ref.[41]); a tree frog's adjustable, impact-resistant toe pads (Adapted from ref.[7]). Corresponding insets show the underlying micro/nanoarchitectures in which the liquid films are infused: patterned radial ridges on the leaf surface (Adapted from ref.[1]); labyrinthine whorls (Adapted from ref.[3]) (top) and villi (Adapted from ref.[8]) (left and bottom) on fish and mammalian cornea; porous cartilage (Adapted from ref.[94]); elastic cuticle network (Adapted from ref.[6]); patterned toe pad structures (Adapted from ref.[7]).

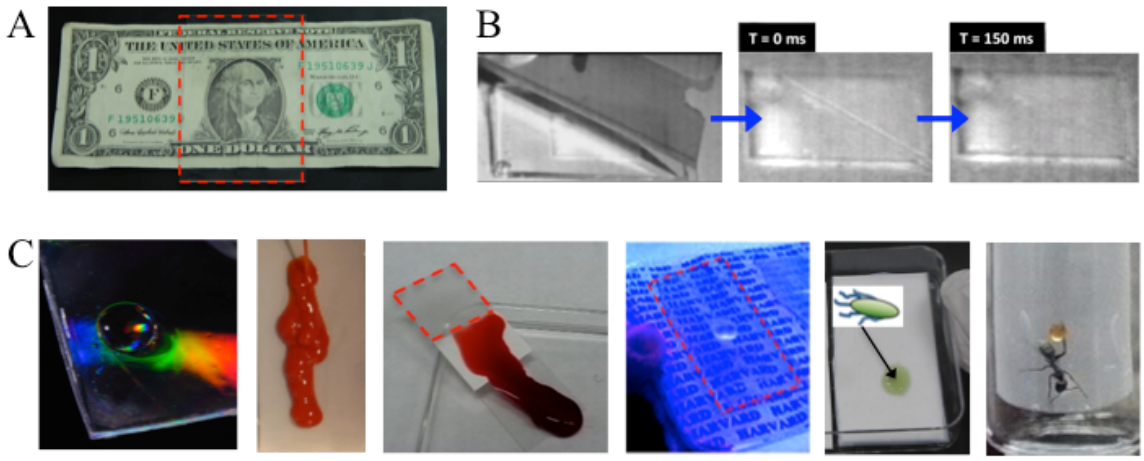


Figure 2. Dynamic perfection. A. A liquid film infused in a rough substrate (red box) flows to form an optically perfect, transparent surface. B. Self-healing liquid surface erases damage within milliseconds. C. Liquid acts as a perfect, defect-free interface toward nearly all substances, solids, and organisms: (from left) liquid droplets of high or low surface tension, ketchup, blood, ice, bacteria and biofilms, and insects cannot adhere, and slide freely off the surface.

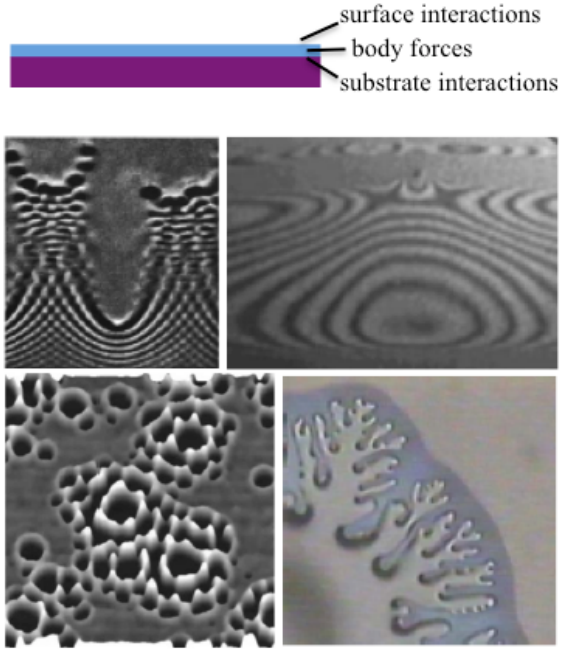


Figure 3. Thin film dynamics arise from complex coupling between substrate, body, and surface forces. Clockwise from top left: patterned liquid motions generated on a flat substrate by gravity (Adapted from ref.[52]); thermocapillary forces (Adapted from ref.[50]);

a substance flowing over the film's surface (Adapted from ref.[53]); and intermolecular interactions with the substrate (Adapted from ref.[51]).

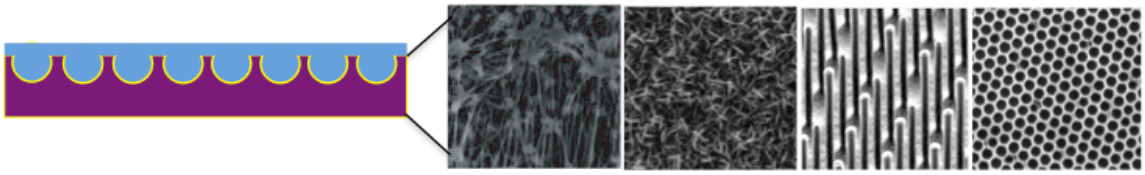


Figure 4. Micro/nanostructuring the substrate. A wide range of 3D architectures can serve as the underlying substrate: (from left) random nanoporous fiber networks; nanocrystalline boehmite; arrays of high aspect ratio nanofibers; inverse colloidal monolayers. All can be chemically functionalized to optimize compatibility with the infusing liquid.

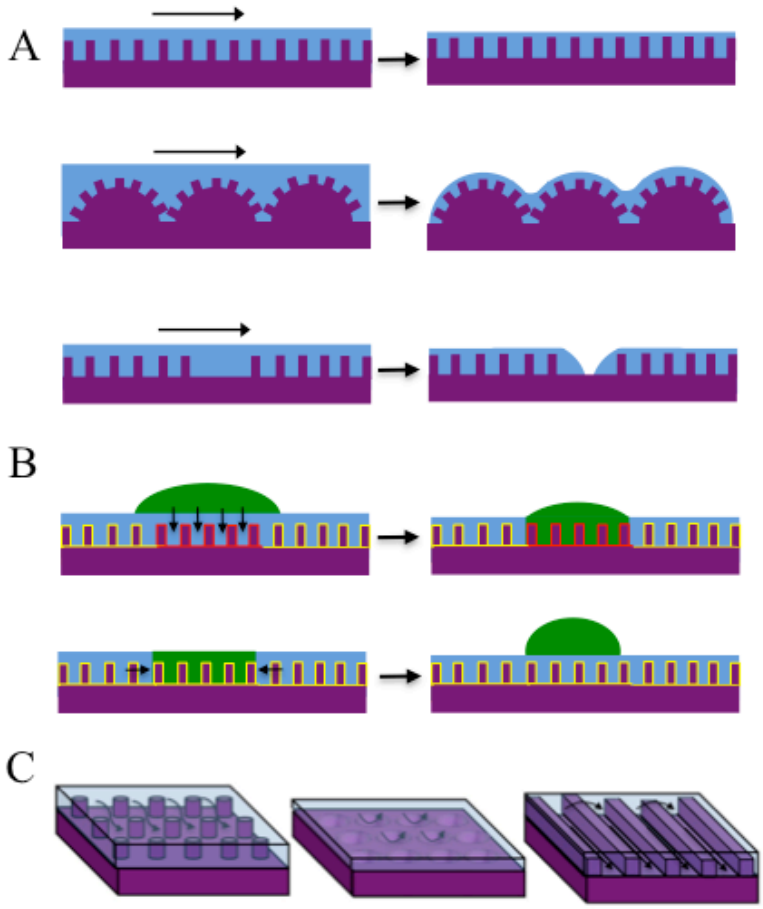


Figure 5. Templating the liquid film's mobility. A. The dimensions and multiscale organization of the underlying architecture create distinct responses to shear force for films infused in: uniform nanostructures (top), microstructures overlaid with nanostructures (center), and uniform nanostructures containing a microscale defect (bottom). B. Combining structure with defined, spatially patterned surface chemistry shapes the film's behavior in the presence of a second fluid, such as how it confines (top) or extrudes (bottom) the second fluid. C. Disconnected surface structures (left), closed-cell pores (center), and parallel ridges (right) create different pathways for flow and large-scale connectivity within and over the surface texture.

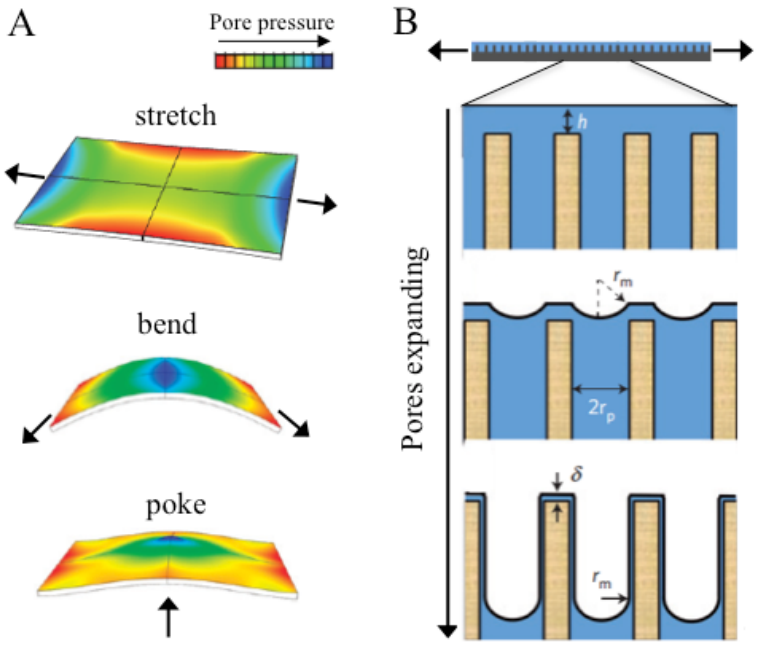


Figure 6. Stimulus-responsive liquid surfaces. A. An elastic structured substrate translates different types of stimuli, such as mechanical stretching, bending, or poking, into characteristic changes in pore pressure across the surface. B. The local pressures cause the liquid surface to curve inward over each pore, creating liquid microtopographies that progressively conform to the underlying architecture as the strain is increased.

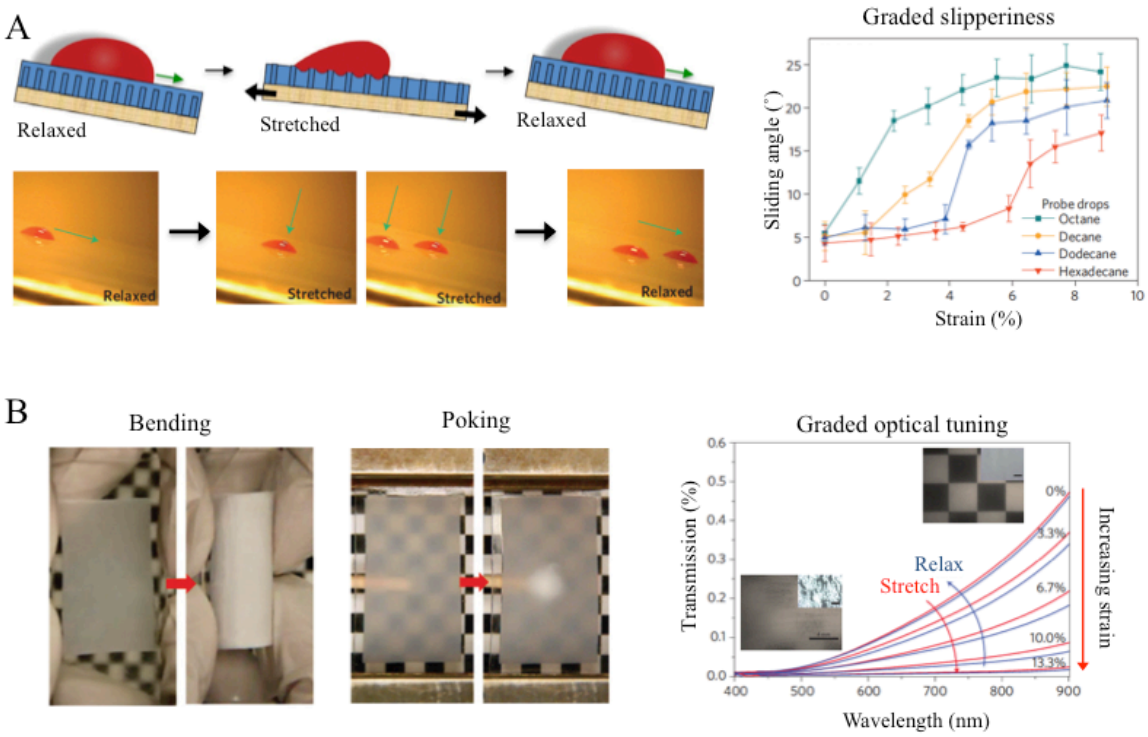
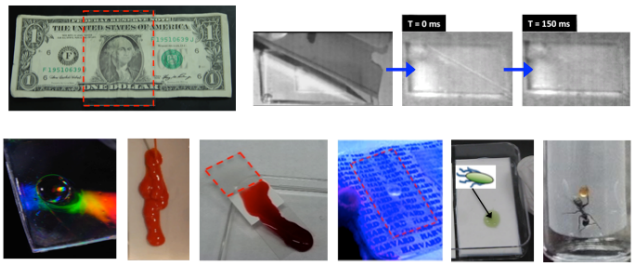


Figure 7. Tunable droplet motion and optics. A. (Left) Stretching roughens the smooth liquid interface, stops a sliding droplet in its tracks, and pins a newly added droplet in place. Relaxing restores the smooth surface and allows both droplets to begin sliding. (Right) The surface slipperiness can be finely tuned by varying the degree of strain, with distinct response profiles for droplets with different interfacial tensions. B. Mechanical stress produces localized (left) and finely graded (right) reversible changes in optical transmission, with decreasing transmission directly correlated with increasing liquid roughness (right, insets).

TOC graphic



Alison Grinthal is a Research Scientist in the School of Engineering and Applied Sciences at Harvard University. Her interests span a wide range of fields, including bioinspired engineering, dynamic and adaptive materials, self-assembly, surface and interfacial phenomena, structure and dynamics of macromolecules, and the interplay between chemistry and mechanics in biological and synthetic systems. She received her B.A. from Swarthmore College in both Chemistry and Anthropology, and received her Ph.D. from Harvard University in Biochemistry.

Joanna Aizenberg is the Amy Smith Berylson Professor of Materials Science and the Director of the Kavli Institute at Harvard University. Her research interests span biomimetics, self-assembly, smart materials, crystal engineering, surface science and biooptics. Aizenberg's select awards include two R&D100 Awards for best technologies of the year and Ronald Breslow ACS Award in Biomimetic Chemistry. Aizenberg is an AAAS and APS Fellow; she has served on the Board of Directors of the MRS.